

SELECTED TRACE METALS IN WATER, SEDIMENT, PLANTS, AND FISH IN RAPID CREEK, RAPID CITY, SOUTH DAKOTA, 1993-94

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CONVERSION FACTORS, ABBREVIATIONS, AND DEFINITIONS OF TERMS

Multiply	By	To obtain
acre-foot (acre-ft)	1,233	cubic meter
cubic foot per second (ft ³ /s)	0.02832	cubic meter per second
foot per mile (ft/mi)	0.1894	meter per kilometer
gram (g)	0.03527	ounce, avoirdupois
liter (L)	0.2642	gallon
microgram (μg)	3.52×10^{-8}	ounce
mile (mi)	1.609	kilometer
milliliter (mL)	0.0338	ounce
millimeter (mm)	0.03937	inch

Water year: In Geological Survey reports dealing with surface-water supply, water year is the 12-month period, October 1 through September 30. The water year is designated by the calendar year in which it ends; thus, the water year ending September 30, 1992, is the "1992 water year."

Sewage Treatment Plant: USGS gaging station names refer to the Rapid City Waste Water Treatment Plant as "Sewage Treatment Plant."

PHYSICAL AND CHEMICAL WATER-QUALITY UNITS

Temperature can be converted to degrees Fahrenheit (°F) or degrees Celsius (°C) by the following equations:

$$^{\circ}\text{F} = 9/5 (^{\circ}\text{C}) + 32$$

$$^{\circ}\text{C} = 5/9 (^{\circ}\text{F} - 32)$$

Specific electrical conductance of water is expressed in microsiemens per centimeter at 25 degrees Celsius (μS/cm). This unit is equivalent to micromhos per centimeter at 25 degrees Celsius.

Micrograms per gram (μg/g) is a weight per weight unit expressing the concentration of a chemical constituent occurring in a solid material. Micrograms per gram is directly equivalent to parts per million, and the terms are used interchangeably in this report.

Milligrams per liter (mg/L) or micrograms per liter (μm/L): Milligrams per liter is a unit expressing the concentration of a chemical constituent in solution as weight (milligrams) of solute per unit volume (liter) of water. One thousand micrograms per liter is equivalent to one milligram per liter. For natural waters with dissolved-solids concentrations less than about 7,000 μg/L, "milligrams per liter" is essentially equivalent to "parts per million" (ppm), and "micrograms per liter" is essentially equivalent to "parts per billion" (ppb); the terms are used interchangeably in this report.

Selected Trace Metals in Water, Sediment, Plants, and Fish in Rapid Creek, Rapid City, South Dakota, 1993-94

By Joyce E. Williamson, Robert M. Goldstein, and Stephen D. Porter

ABSTRACT

Local industries in Rapid City have reported violations of maximum contaminant levels for their National Pollutant Discharge Elimination System permits. The industries initiated a request that the City of Rapid City investigate whether natural concentrations of trace metals in the municipal water supply were contributing to concentrations of trace metals in their industrial effluent. Metals of specific concern were silver, cadmium, copper, and zinc. Stream-water, bed-sediment, plant, and fish sampling was conducted in an effort to better understand the aquatic conditions of Rapid Creek.

Within Rapid Creek, concentrations of silver, cadmium, copper, and zinc in stream water increased from upstream to downstream of the wastewater treatment plant. Silver concentrations were below the laboratory reporting limits for all samples with the exception of the effluent discharge and immediately downstream in Rapid Creek. Cadmium concentrations were at or below the laboratory reporting limit for all sites. Copper and zinc concentrations were detectable at all stream sites and two wells but not at a spring site. Concentrations of silver, cadmium, copper, and zinc in bed-sediment samples all increased from upstream to downstream of the wastewater treatment plant. Concentrations of silver, cadmium, copper, and zinc in plant-tissue samples all increased from upstream to downstream of the wastewater treatment plant and were consistent with increased concentrations in both water and

bed sediments. Silver concentrations in fish-liver samples were smaller upstream compared to downstream of the wastewater treatment plant; cadmium concentrations varied little between sites. Copper and zinc concentrations in fish-liver samples were larger upstream compared to downstream of the plant.

Based on the limited sampling during this study, there is evidence that the selected metals present in both the water and bed sediments are bioaccumulating in the plant and fish species. Results also indicate that biomagnification in the plants and fish is not occurring; that is, the concentrations found in the sediment, plants, and fish are all at about the same order of magnitude.

Based on the concentrations found in the stream-water, bed-sediment, plant, and fish sampling, there is an increase in the mean concentrations of selected trace metals from upstream of Rapid City to downstream of where the treatment plant effluent enters. Increases in concentrations from immediately upstream to downstream of the wastewater treatment plant are consistent with concentrations added by the wastewater treatment plant effluent. Bed-sediment concentrations of silver and cadmium increased between the two upstream sites and additional sampling would be necessary to determine possible point sources of trace metals in Rapid Creek upstream of the wastewater treatment plant. Exceptions to increasing concentrations were copper and zinc in fish-liver tissue, which decreased from upstream to downstream of the wastewater treatment plant effluent.

INTRODUCTION

In an effort to control water pollution, Congress passed the Federal Water Pollution Control Act (Public Law 92-500) in 1972. Congress amended the law in 1977, changing the name to the Clean Water Act. Section 402 of the Act, administered by the U.S. Environmental Protection Agency (EPA), establishes the procedure for obtaining National Pollutant Discharge Elimination System (NPDES) permits to discharge into streams (Ward, 1982). These permits include both industrial and wastewater discharges and focus on protection of aquatic life. An NPDES permit requires that conditions of sections 301, 302, 306, 307, 308, and 403 of the Act be met by the permittee (Ward, 1982). These sections address effluent limitations; water-quality-related effluent limitations; national standards of performance; toxic and pretreatment effluent standards; inspections, monitoring and entry strategies; and discharge criteria. The State of South Dakota is authorized to implement the NPDES program for industrial and wastewater discharges. As part of this authorization, the State has classified each South Dakota stream with regard to use and has established water-quality criteria to meet those uses (South Dakota Department of Water and Natural Resources, 1987). The NPDES permitting program is a means of implementing the Surface Water Quality Standards adopted by the State of South Dakota.

Background

Various industries within Rapid City have NPDES permits to discharge into the City sanitary-sewer system, which discharges to Rapid Creek. The maximum effluent limits established for the industries are indirectly based upon the water-quality criteria for Rapid Creek. Some of these industries are required to pretreat and to periodically monitor their effluent prior to discharge into the City sanitary-sewer system. These industries have recovery systems in place to remove the majority of metals from their effluent. The City regularly monitors the effluent for a range of constituents as required by the NPDES permits and occasionally collects unscheduled samples.

In 1990, exceedances of maximum contaminant levels were found by a few local industries and reported to the City. Two industries sampled the City tap water at their places of business and reported detectable concentrations of silver, copper, and zinc.

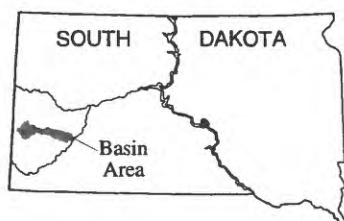
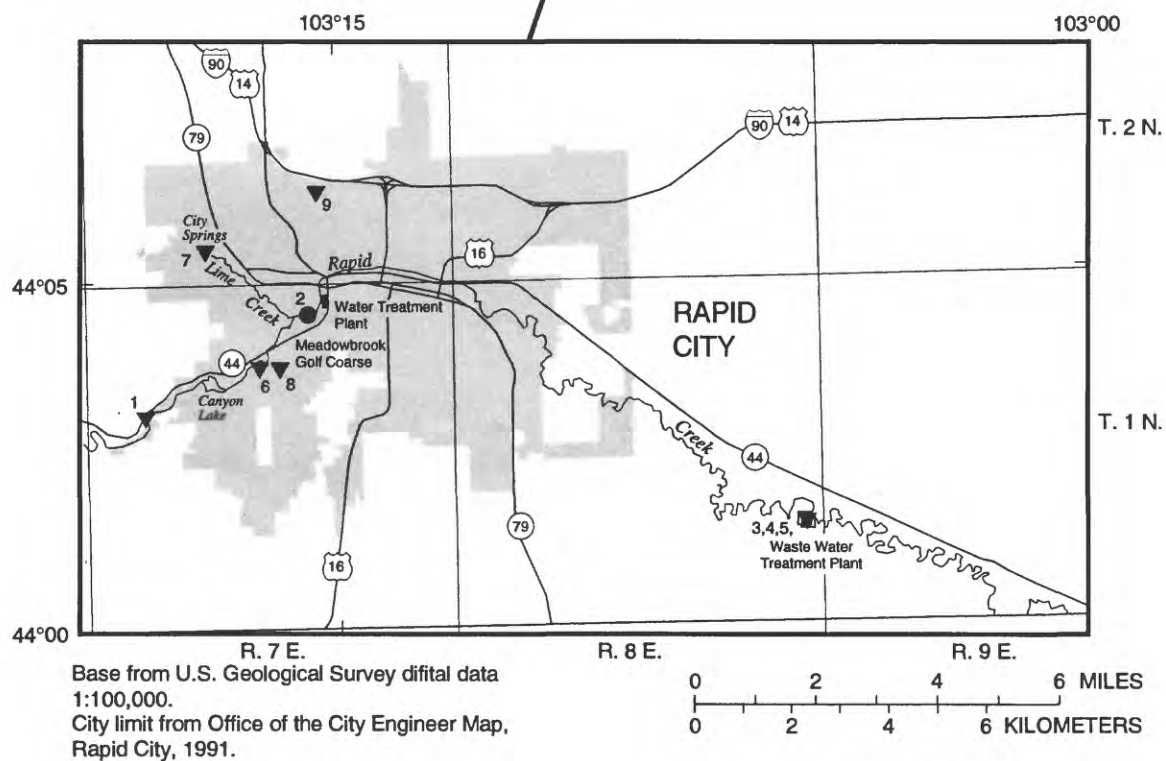
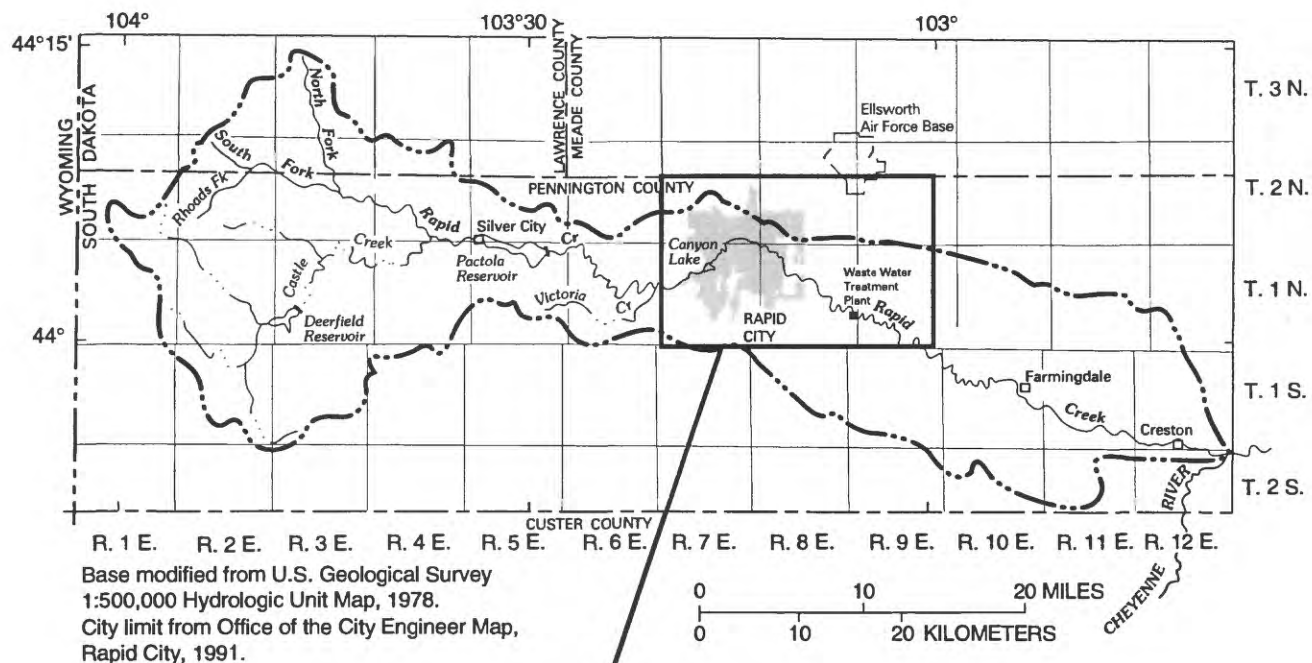
The industries subsequently requested that the City investigate whether natural concentrations of trace metals in the municipal water supply were contributing to concentrations of trace metals in the industrial effluent.

Following this request, the City began collecting monthly water samples from May 1991 to May 1992 at selected locations along Rapid Creek from upstream of Pactola Reservoir near Silver City to downstream of where the City's wastewater treatment plant (WWTP) effluent enters the creek (fig. 1). Concentrations of trace metals in these samples were found to be as much as 66 µg/L of silver, 7 µg/L of cadmium, 22 µg/L of copper, and 236 µg/L of zinc (Chuck Larson, City of Rapid City, written commun., 1992).

Based on these preliminary findings, the City considered petitioning the State of South Dakota for a modification of aquatic standards for Rapid Creek. The EPA has established procedures necessary to establish criteria for the protection of aquatic life (U.S. Environmental Protection Agency, 1985). The State of South Dakota has adopted the EPA standards for trace metals in Rapid Creek. These standards are based on results from laboratory experiments conducted under controlled conditions (U.S. Environmental Protection Agency, 1992). Differences between Rapid Creek and the laboratory waters used to establish the standards could result in a situation where the current standards may be too lenient to protect the aquatic life or may be more stringent than necessary. The NPDES limits can be modified to reflect naturally occurring concentrations of trace metals in the stream. Methods for modification of criteria are in place (U.S. Environmental Protection Agency, 1983) and additional guidelines specifically pertaining to metals are available (U.S. Environmental Protection Agency, 1992). Requirements for the modification of criteria include a good understanding of the stream and supporting data to ensure that the aquatic life will be protected.

Purpose and Scope

During 1991, Rapid City Public Works staff approached the U.S. Geological Survey (USGS) for assistance in determining background concentrations of trace metals in Rapid Creek. Elements of particular concern were silver, cadmium, copper, and zinc. Stream-water, bed-sediment, plant, and fish sampling was conducted at four sites along Rapid Creek in an effort to better understand the aquatic conditions of



- EXPLANATION**
- BASIN BOUNDARY
 - ▼ 9 WATER-QUALITY SITE--Number indicates site identification
 - 2 SEDIMENT AND PLANT SITE--Number indicates site identification
 - 3 WATER-QUALITY, SEDIMENT, PLANT, AND FISH SITE--Number indicates site identification

Figure 1. Location of sampling sites within Rapid Creek Basin.

Rapid Creek. Additional water-quality samples were collected for WWTP effluent, at two wells that are part of the City water supply, at one of the City's infiltration galleries that supply water from the Rapid Creek alluvium, and at a spring within the City that had detectable levels of silver during earlier sampling under different sampling and laboratory methods. The spring discharges from the same aquifer that is a major source to the City's water-supply system. This report describes the results of this sampling and possible effects on plants and fish of the levels of the trace metals that were determined.

Description of Study Area

Rapid City is located on the eastern flank of the Black Hills uplift. Rapid Creek (fig. 1) is a perennial stream that originates on the core of the uplift, which generally is composed of Precambrian igneous and metamorphic rocks (Greene, 1993). The reach of Rapid Creek from Pactola Reservoir to within Rapid City has an average gradient of 48 ft/mi; is characteristic of a mountain stream with a sand, gravel, and cobble bottom; and crosses a series of outcrops of sedimentary rocks, which are predominately sandstones and limestones. These sedimentary rocks contain abundant calcite, dolomite, and anhydrite that contain calcium and magnesium (Peter, 1985). Rapid Creek downstream of Pactola Reservoir generally has very hard water, which is defined as over 180 mg/L hardness expressed as calcium carbonate (Freeman and Komar, 1991). In addition, various naturally occurring trace metals are available within the entire basin for dissolution and transport by the stream. The reach from Rapid City to the confluence with the Cheyenne River near Creston has an average gradient of 13 ft/mi and is characteristic of a meandering prairie stream with a mud bottom (Goddard and others, 1989).

Pactola Reservoir, which has a conservation capacity of 54,955 acre-ft, regulates the flow in Rapid Creek. The average annual streamflow of Rapid Creek below Pactola Dam is 29,380 acre-ft (1957-94) (U.S. Geological Survey, 1995), and the general water quality (specific conductance, pH, hardness, major ions, nutrients) of flows discharged from Pactola Reservoir generally has little monthly variation (Freeman and Komar, 1991). Roads and small communities located along Rapid Creek from Pactola Reservoir to Rapid City affect the stream with inputs from road sediments, salts, oils and greases, and localized septic

systems. Within Rapid City, Rapid Creek is affected by numerous factors, including snowmelt and stormwater runoff from urban roads; various domestic, municipal, and minor irrigation diversions and return flows; and numerous point and nonpoint sources of inflow. Between the eastern edge of Rapid City downstream to the WWTP, stream quality is affected by significant irrigation diversions and return flows; runoff from roads, suburban areas, and agricultural areas; and numerous septic systems within the flood plain.

Mean monthly flow (1957-94) at USGS gaging station 06411500, Rapid Creek below Pactola Reservoir, varies seasonally from a minimum of 16.1 ft³/s in January to a maximum of 82.7 ft³/s in June. Many losses and gains occur on Rapid Creek between Pactola Reservoir and its mouth because of aquifer recharge zones, irrigation diversions and return flows, springs, tributaries, drainage ditches, and the City WWTP effluent. The mean monthly discharge (1957-94) at USGS gaging station 06421500, Rapid Creek near Farmingdale (67 river miles downstream of Pactola Reservoir), varies from a minimum of 31.7 ft³/s in August to a maximum of 116 ft³/s in June (U.S. Geological Survey, 1995).

The South Dakota Department of Environment and Natural Resources has classified all streams in South Dakota for beneficial use relating to wildlife propagation, stock watering, and irrigation. The reach of Rapid Creek from Pactola Reservoir to upstream of the WWTP effluent is classified as a cold-water permanent fishery and fish-life propagation; it also is classified as suitable for both limited contact and immersion recreation. The downstream reach from upstream of the WWTP effluent to the confluence with the Cheyenne River is classified as a warm-water semipermanent fishery. The downstream reach also is classified as suitable for both immersion and limited-contact recreation for 5 months from May through September when chlorine is added at the WWTP.

Acknowledgments

Many people provided technical and professional assistance during the course of this study. A good working relationship was maintained throughout the study with the City, the South Dakota Department of Environment and Natural Resources, and the U.S. Environmental Protection Agency. The input and guidance from these agencies is much appreciated.

SAMPLING SITES AND METHODS

Samples were collected for analysis of trace metals in the stream water, bed sediment, plants, and fish. Water-quality samples were collected to determine concentrations, ratios, and variances of total and dissolved concentrations in the stream water column if detectable levels were found. Bed-sediment samples were collected to determine levels available to plants and aquatic life. Plants and fish were sampled to determine if and at what levels the trace metals were being taken up by the aquatic life within the stream.

For all samples, concentrations of silver, cadmium, copper, and zinc were determined. Concentrations of other selected constituents of interest were determined for the water-quality samples. These constituents and properties included chloride, which in excess of 35 mg/L may be related to silver solubility, and hardness, which is used to establish the acute toxicity criteria for silver, cadmium, copper, and zinc (U.S. Environmental Protection Agency, 1980). Common cations, anions, field pH, and field specific conductance also were determined. Additional trace metals were analyzed as part of the laboratory

processing. These data are presented in the tables in the Supplemental Data section at the end of this report.

Sites

Water-quality samples were collected at eight sites along or near Rapid Creek (fig. 1, table 1). These sites included a background site on Rapid Creek located upstream of Rapid City (site 1), a site on Rapid Creek immediately upstream of the WWTP (site 3), the WWTP effluent (site 4), a site on Rapid Creek immediately downstream of the WWTP (site 5), an infiltration gallery in the Rapid Creek alluvial aquifer (site 6), a spring discharging from the Madison aquifer (site 7), and two wells completed in the Madison aquifer (sites 8 and 9). The WWTP effluent was sampled to obtain concentrations from a known source of trace metals to the stream. The infiltration gallery and wells were sampled to provide information on inputs to the City's water supply from these sources. Although the spring (site 7) is not a part of the City's supply system, it originates from the same formation (Madison Limestone) as the wells, and samples collected at this spring during a prior study had detectable concentrations of silver.

Table 1. Site information and types of sampling conducted along or near Rapid Creek

[--, not applicable]

Site number	USGS site identification number	River mile	Site name	Latitude	Longitude	Type of sampling
1	06412500	84.4	Rapid Creek above Canyon Lake, near Rapid City	440310	1031841	Water quality
2	06413700	80.1	Rapid Creek above Water Treatment Plant, at Rapid City	440429	1031534	Bed sediment, plants
3	440126103054701	61.6	Rapid Creek above Sewage Treatment Plant, near Rapid City	440126	1030547	Water quality, bed sediment, plants, fish
4	440124103054601	60.5	Sewage Treatment Plant effluent near Rapid City	440124	1030546	Water quality
5	06418900	60.4	Rapid Creek below Sewage Treatment Plant, near Rapid City	440124	1030543	Water quality, bed sediment, plants, fish
6	440343103163002	--	Meadowbrook gallery at number 4 pumphouse	440343	1031630	Water quality
7	06413600	--	City Springs at Rapid City	440524	1031732	Water quality
8	440342103160701	--	Well RC 9 completed in the Madison aquifer	440342	1031607	Water quality
9	440612103152001	--	Well RC 10 completed in the Madison aquifer	440612	1031520	Water quality

Bed-sediment samples were collected at sites 2, 3, and 5. Site 2 was used instead of site 1 to obtain enough fine-grained sediment for sampling, remaining as close to site 1 as possible. Plant samples were collected at the same sites used to collect bed-sediment samples (sites 2, 3, and 5). Fish were collected from a 0.6-mi reach of the stream from about 2.5 mi to 3.1 mi upstream of where WWTP effluent enters Rapid Creek and from a 1.6-mi reach of the stream immediately downstream of where WWTP effluent enters Rapid Creek.

Methods

Water-quality samples were collected in downstream order, with the exception of samples collected immediately upstream and downstream of the WWTP effluent (sites 3 and 5). Because the sites where the effluent enters are so close to one another, the downstream samples were collected first to avoid disturbances from collecting the upstream samples.

Recent research indicates that many reported trace-element concentrations are not accurate because of contamination during field sampling and processing (Windom and others, 1991). Proper collection, documentation, and quality-assurance samples are necessary at the part-per-million (essentially equal to milligrams per liter) and part-per-billion (essentially equal to micrograms per liter) reporting levels. Therefore, water-quality samples were collected using low-level, ultra-clean methods developed to eliminate as many sources of sample contamination as possible and described by Horowitz and others (1994).

Prior to sampling, all water and sediment-sampling equipment was presoaked in a Liquinox solution, thoroughly scrubbed, rinsed with tap water, and soaked in a 5-percent hydrochloric acid solution. Equipment was then rinsed three times with deionized water and placed in sealable plastic bags until use. During sampling and processing, non-powdered vinyl gloves were worn to reduce contamination from human contact. Two people worked together to collect and process the samples, enabling one sampler to avoid contact with possible contamination sources. Samples were protected from outside sources as much as possible throughout the collection and processing steps. After samples were collected, filtered if applicable, and preserved, they were shipped to the USGS National Water Quality Laboratory (NWQL) for analysis.

High-flow samples were collected to determine concentrations in the stream water column after a selected storm event. Flows ranged from 194 to 207 ft³/s for the high-flow events. Low-flow 24-hour samples were collected to determine diurnal concentration variations in the water column, with flows ranging from 30 to 49 ft³/s.

Bed-sediment samples (sites 2, 3, and 5) were collected along inside bends and bars where fine-grained sediment had settled. One sample was collected at site 2 where fine-grained sediments were scarce, and three samples were collected from sites 3 and 5. Each sample consisted of the top 2 to 3 in. of bed sediment and was collected from a different sampling location in the stream reach. The downstream samples were collected first to avoid disturbances from collecting the upstream sample. Samples were collected with a polyethylene scoop and placed in pre-cleaned glass containers. Samples were subsequently wet-sieved through a 0.062-mm mesh polyethylene sieve using a minimal amount of filtered stream water. After sieving, samples were placed in 500 mL Teflon bottles. The sample from site 2 and one sample from site 5 were split and processed as quality-assurance samples. After settling for 24 hours, samples were decanted and shipped to the USGS Branch of Geochemistry, Analytical Chemistry Services (GACS) Group, for further processing and analysis.

Plant samples were collected at the same three sites as the bed-sediment samples (sites 2, 3, and 5). Leafy pond weed (*Potamogeton foliosus*) was collected at site 2 and Sago pond weed (*Potamogeton pectinatus*) was collected at sites 3 and 5. Only one plant sample was collected at site 2 due to lack of abundance; three plant samples each were collected at site 3 and at site 5. Plants were collected by wading the stream and pulling the plants from the streambed in order to collect as much of the whole plant as possible, including roots. An effort was made to collect each sample from a separate area within the stream. The plants were rinsed in stream water to remove as much sediment and debris as possible and placed in a plastic bucket previously rinsed with stream water. Then the plants were placed in sealable plastic bags and cooled for further cleaning in the office laboratory. Office laboratory cleaning consisted of some additional washing of each plant with tap water to remove any remaining debris, sediment, and plants other than the pond weed. Any addition of metals by the tap water would be minimal compared to expected high metal concentrations

in sediments that would be left on plants without thorough rinsing. The samples were dried on paper towels, placed in sealable plastic bags, weighed, packed on dry ice, and sent to the GACS for analysis.

Fish samples were collected by electrofishing with a backpack shocker. One person waded the stream with the shocker, followed by a second person with a net to collect stunned fish, and a third person with plastic buckets of stream water to revive the fish. Only white sucker (*Castostomus commersoni*) were saved from the collection process; other species were returned to the stream. Fifteen white suckers were collected from each site and divided into three size groupings for composite samples (five fish per size composite). The fish were dissected and liver tissue was collected for laboratory analysis. Weight, length, sex, and any abnormalities also were noted. The liver tissue was placed in a sealable plastic bag, placed on dry ice, and shipped to the NWQL for analysis.

Bed-sediment samples, plant-tissue samples, and fish-tissue samples were grouped for statistical comparisons as either upstream of the WWTP or downstream of the WWTP. Statistical comparisons were made using the Wilcoxon rank-sum test, also known as the Mann-Whitney test. This is a nonparametric test used to determine if the two groups are from the same population using a significance level of 0.10. This test does not require that the distribution of the sample sets be normal (Helsel and Hirsch, 1992). Thus, the Wilcoxon rank-sum test is better suited for comparison of small sample sets than parametric tests are.

Various quality assurance (QA) samples were collected throughout the sampling process to ensure high-quality data and the validity of values obtained from sampling. Quality control (QC) consisted of using precleaned, separate sampling devices whenever possible. When this was not possible, the sampling device was cleaned between samples and a field blank was taken to confirm that the device was clean prior to sampling the next site. Equipment blanks and field blanks were collected to test the cleanliness of the equipment. Equipment blanks are collected in the laboratory; field blanks are collected at the sampling site. Equipment blanks were collected prior to water-quality sampling, and field blanks were collected when on-site cleaning took place. Splits are two samples processed from the same collection of water or bed sediment and are used to determine any field processing or laboratory variance. The QA/QC for water-quality samples included equipment blanks both prior to sampling and

between sites in addition to splits of actual samples taken. The QA/QC for bed-sediment sampling consisted of a split as a verification of laboratory results. The QA/QC for fish samples consisted of analysis for aluminum, which normally should not be found in fish liver at levels above the parts per million (ppm) level (Spry and Wiener, 1991). Concentrations above this level would indicate contamination from outside sources.

CONCENTRATIONS OF SELECTED TRACE METALS

Water-quality samples were collected at four sites along Rapid Creek (sites 1, 3, 4, and 5) and at four additional sites consisting of an infiltration gallery (site 6), a spring (site 7), and two wells (sites 8 and 9). Concentrations of total recoverable and dissolved silver, cadmium, copper, and zinc are summarized in table 2. All of the water-quality data are presented in table 4 in the Supplemental Data section.

The high-flow and low-flow 24-hour samples were evaluated to determine if concentration levels were a function of flow conditions or diurnal variations in the stream. Those samples did not provide any additional insights, although additional sampling would be necessary to reach a definite conclusion concerning the relation between concentration levels and other variables.

Concentrations of silver were below the laboratory reporting limits of 1.0 µg/L (total recoverable) and 0.2 µg/L (dissolved) for all samples collected from Rapid Creek upstream of the WWTP (sites 1 and 3), the infiltration gallery (site 6), the spring (site 7), and the two wells (sites 8 and 9). Concentrations of silver were detected in the WWTP effluent (site 4) and in Rapid Creek downstream of the WWTP (site 5). Cadmium was detected (0.1 µg/L) only at site 1 during a high-flow event on July 6, 1993, and in the WWTP effluent (site 4). Copper was detected occasionally at all sites except the spring (site 7), with larger concentrations in Rapid Creek within and downstream of the WWTP effluent (sites 4 and 5). Samples from the upstream sites generally had concentrations less than 3 µg/L. Zinc was detected at all sites except the spring (site 7), again with larger concentrations within and downstream of the WWTP effluent. Both copper and zinc were found in all of the municipal water-supply sources tested (sites 6, 8, and 9).

Table 2. Concentrations of silver, cadmium, copper, and zinc in stream-water samples

[µg/L, micrograms per liter]

Site number	Date	Time	Silver total recoverable (µg/L as AG) (01077)	Silver, dissolved (µg/L as AG) (01075)	Cadmium, total recoverable (µg/L as CD) (01027)	Cadmium, dissolved (µg/L as CD) (01025)	Copper, total recoverable (µg/L as CU) (01042)	Copper, dissolved (µg/L as CU) (01040)	Zinc, total recoverable (µg/L as ZN) (01092)	Zinc, dissolved (µg/L as ZN) (01090)
1	07-06-93	0845	<1	<0.2	<1	0.1	1	<1	<10	<1
	01-24-94	0700	<1	<0.2	<1	<0.1	<1	<1	<10	<1
	01-24-94	1100	<1	<0.2	<1	<0.1	<1	<1	<10	3
	01-24-94	1500	<1	<0.2	<1	<0.1	<1	<1	<10	1
	01-24-94	1900	<1	<0.2	1	<0.1	<1	<1	<10	1
	01-24-94	2300	<1	<0.2	<1	<0.1	<1	<1	<10	3
	01-25-94	0300	<1	<0.2	<1	<0.1	<1	<1	<10	3
	08-22-94	0745	<1	<0.2	<1	<0.1	<1	<1	<10	1
3	07-06-93	1145	<1	<0.2	<1	<0.1	3	<1	10	<1
	01-26-94	0700	<1	<0.2	<1	<0.1	<1	<1	<10	1
	01-26-94	1100	<1	<0.2	<1	<0.1	<1	<1	<10	1
	01-26-94	1500	<1	<0.2	<1	<0.1	<1	<1	<10	2
	01-26-94	1900	<1	<0.2	<1	<0.1	<1	<1	<10	5
	01-26-94	2300	<1	<0.2	<1	<0.1	<1	<1	<10	2
	01-27-94	0300	<1	<0.2	<1	<0.1	<1	<1	<10	1
	08-24-94	1345	<1	<0.2	<1	<0.1	<1	1	20	<1
	10-06-94	0930	<1	<0.2	<1	<0.1	2	<1	<10	3
4	08-24-94	0915	5	2.4	<1	0.1	16	13	40	29
5	08-24-94	0730	<1	0.3	--	<0.1	4	4	10	5
	10-06-94	0730	1	0.5	<1	<0.1	9	5	<20	14
6	08-22-94	1145	<1	<0.2	<1	<0.1	11	2	<10	1
7	07-08-94	1340	<1	<0.2	<1	<0.1	<1	<1	<10	<1
8	08-25-94	1145	<1	<0.2	<1	<0.1	3	3	<10	5
9	08-25-94	1315	<1	<0.2	<1	<0.1	21	2	10	10

Bed-sediment samples were collected at three sites along Rapid Creek. One sample was collected at site 2, three samples at site 3, and three samples at site 5 (fig. 2). Chemical analyses of bed sediments are presented in table 5 in the Supplemental Data section.

Silver concentrations in bed sediments increased downstream with a slight increase from 0.18 µg/g at site 2 to an average of 0.37 µg/g at site 3 and then a much larger increase to an average of 11.9 µg/g at site 5 (fig. 2). The substantial increase from site 3 to site 5 is consistent with the addition of silver by the WWTP effluent (site 4, table 2). The slight increase between site 2 and site 3 may be an indication of background levels of silver or of possible low-level, non-

point sources of silver entering this reach of the stream. Cadmium concentrations increased slightly from upstream to downstream, although not as much as for the other trace metals; water-quality sampling indicated that very little cadmium was being added by the WWTP effluent. Copper concentrations were approximately the same at both sites upstream of the WWTP effluent (sites 2 and 3) and increased substantially between sites 3 and 5. Zinc concentrations were approximately the same at both sites upstream of the WWTP effluent (sites 2 and 3), and increased between sites 3 and 5. The increases in concentrations of copper and zinc from site 3 to site 5 are consistent with the addition of copper and zinc by the WWTP effluent

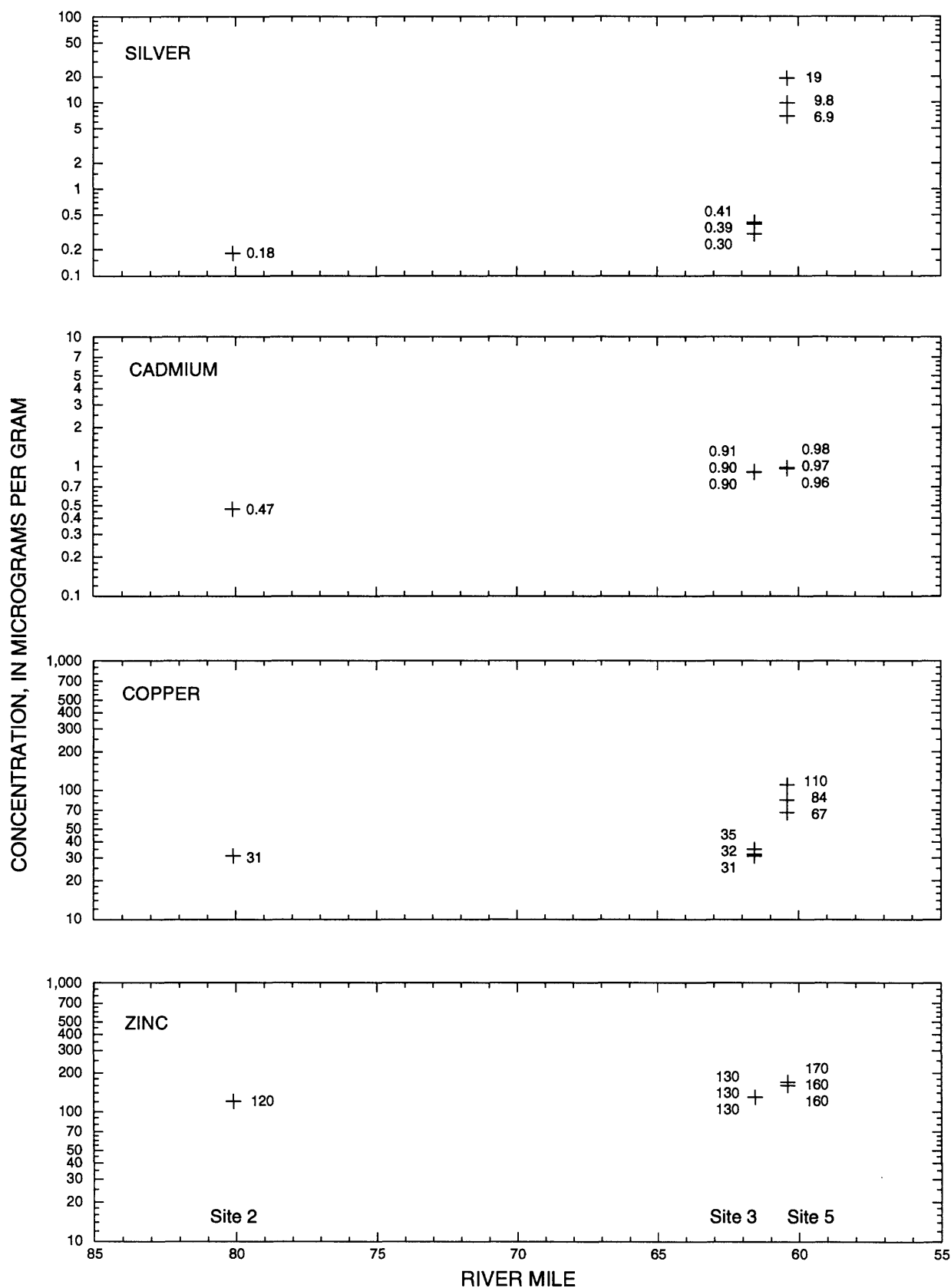


Figure 2. Concentrations of silver, cadmium, copper, and zinc in bed sediments (site 4, Waste Water Treatment Plant effluent enters stream at river mile 60.5).

(table 2). Concentrations of each of the four selected trace metals in bed sediments were statistically smaller upstream of the WWTP effluent than downstream of the WWTP effluent ($p=0.029$ for all four tests, sites 2 and 3 compared to site 5, Wilcoxon rank-sum test).

Plant-tissue samples also were collected at three sites along Rapid Creek (sites 2, 3, and 5). Plant-tissue samples consisted of one sample collected at site 2 (limited plant species available), three samples at site 3, and three samples at site 5 (fig. 3). Chemical analyses of plant tissues are presented in table 6 in the Supplemental Data section.

Silver concentrations in plants collected at sites 2 and 3 were less than the laboratory reporting limit of $0.2 \mu\text{g/g}$. Concentrations of silver in plants collected downstream of the WWTP effluent ranged from 4.2 to $5.5 \mu\text{g/g}$, and averaged $5.0 \mu\text{g/g}$. Concentrations of cadmium, copper, and zinc also increased from site 3 upstream of the WWTP to site 5 downstream of the WWTP, which is consistent with increased concentrations in both water and bed sediments between these two sites. Concentrations of silver, cadmium, copper, and zinc in plant-tissue samples were statistically smaller upstream of the WWTP effluent than downstream of the WWTP effluent ($p=0.050$ for all four tests, site 3 compared to site 5). Concentrations of cadmium, copper, and zinc all tended to be comparatively high at site 2, which could be because the plants are from the leafy pond weed rather than the Sago pond weed at sites 3 and 5. Therefore, site 2 was not used in the statistical analysis.

Three fish samples were collected at two sites along Rapid Creek (sites 3 and 5) and liver tissue was analyzed for trace metals (fig. 4). Samples collected were composites of liver tissue from five fish of approximately the same size (age). Mean fish weights and lengths are presented in table 3. Chemical analysis of fish-liver tissue are presented in table 7 in the Supplemental Data section.

Silver concentrations in fish-liver tissue generally were smaller upstream of the WWTP effluent than downstream of the WWTP effluent, with the largest concentration measured upstream being equal to the smallest concentration downstream. Concentrations of silver in fish-liver tissue samples were statistically smaller upstream of the WWTP effluent than downstream of the WWTP effluent ($p=0.075$). Concentrations of cadmium were not significantly different between sites 3 and 5 ($p=0.15$). Copper and zinc concentrations in fish liver were larger upstream of the WWTP effluent than downstream of the WWTP effluent, with some overlap in ranges for copper. Copper and zinc are necessary metabolic requirements and are almost always observed at tissue concentrations much greater than other trace elements (Lagler and others, 1962). Although excess zinc in water can cause direct toxicity to aquatic organisms, zinc in low concentrations is an essential dietary element for animal and plant life (Keller, 1988). Concentrations of copper and zinc in fish-liver tissue samples were statistically greater upstream of the WWTP effluent than downstream of the WWTP effluent ($p=0.10$ and $p=0.05$, respectively).

The QA/QC results are presented in table 4 (water quality), table 5 (bed sediments), and table 7 (fish-liver tissue) of the Supplemental Data section. The QA/QC for fish tissue included an analysis for aluminum. As previously indicated, aluminum found in fish liver at levels above the parts per million level would indicate contamination from outside sources (Spry and Wiener, 1991). One detection of $11 \mu\text{g/g}$ of aluminum for site 3 possibly is the result of field contamination during sample collection or processing. However, because the values for silver, cadmium, copper, and zinc were lower or between concentrations from uncontaminated samples, the data were not excluded.

Table 3. Mean weight and length for fish sampled in Rapid Creek upstream and downstream of the wastewater treatment plant

Category of fish size (n=5 for each category)	Upstream of the wastewater treatment plant effluent				Downstream of the wastewater treatment plant effluent			
	Weight, in grams		Length, in millimeters		Weight, in grams		Length, in millimeters	
	Mean	Standard deviation	Mean	Standard deviation	Mean	Standard deviation	Mean	Standard deviation
Small	154	11.5	245	10.4	134	12.2	226	6.5
Medium	279	30.6	298	8.9	356	10.2	308	4.9
Large	503	33.2	355	6.0	675	35.1	378	6.6

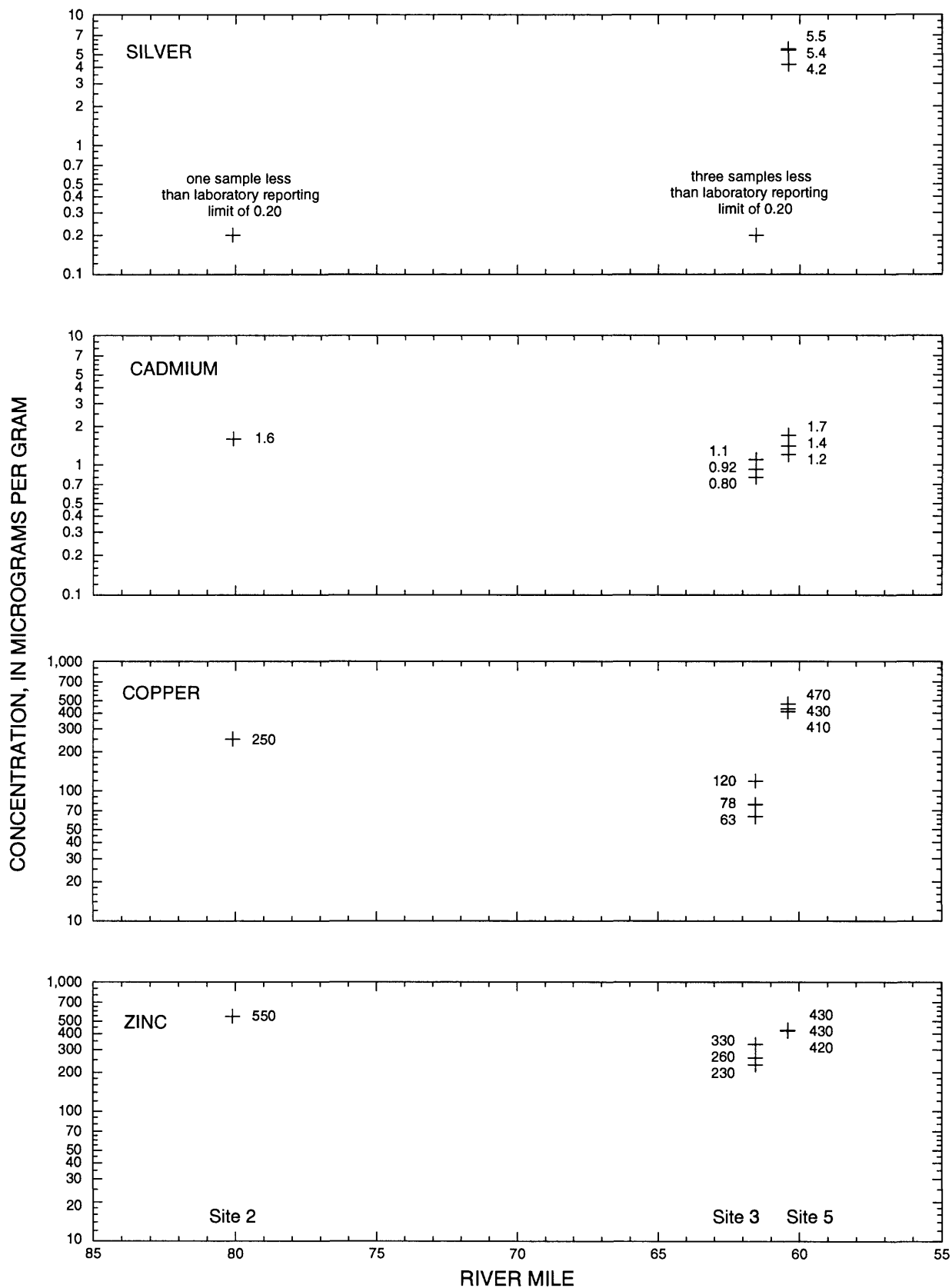


Figure 3. Concentrations of silver, cadmium, copper, and zinc in plant tissue (site 4, Waste Water Treatment Plant effluent enters stream at river mile 60.5).

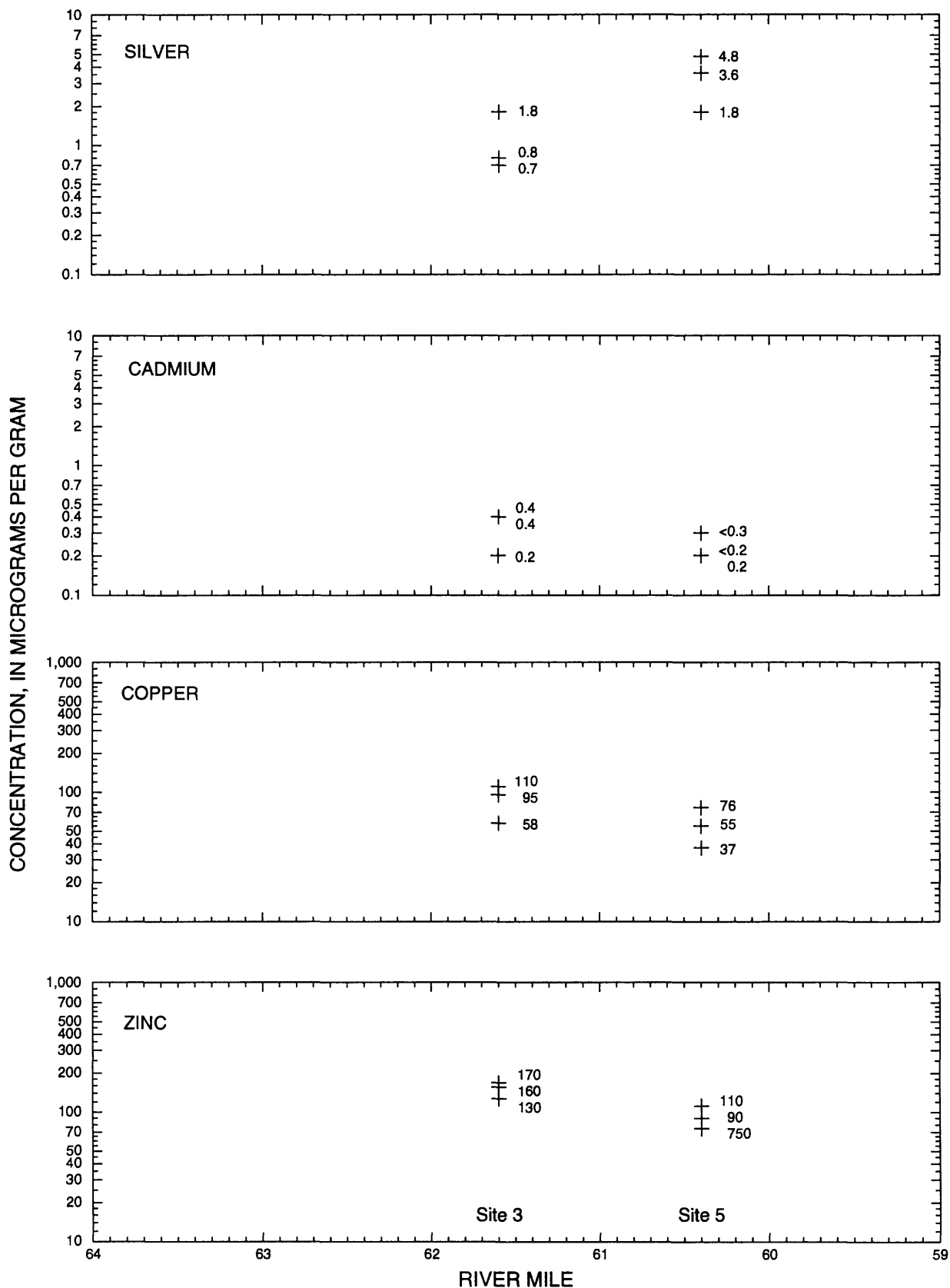


Figure 4. Concentrations of silver, cadmium, copper, and zinc in fish-liver tissue (site 4, Waste Water Treatment Plant effluent enters stream at river mile 60.5).

EFFECTS OF SELECTED TRACE METALS ON PLANTS AND FISH

Biological sampling took place in early October 1994 when streamflow was low, but prior to freezing temperatures that would reduce plant growth. Biological sampling primarily was done immediately upstream of the WWTP effluent (site 3) and immediately downstream of the WWTP effluent (site 5), with three samples collected at each of the respective sites. The biological sampling was done to provide information on the concentrations and accumulation of silver and other trace metals in the biota and was not intended to answer all questions regarding the biological health of the stream. Bioaccumulation is the process by which chemicals are taken up by plants and other aquatic organisms either directly from the water or through consumption of food. Trace metals would be available to aquatic plants from both water and sediments and available to fish from water, sediments, and plants. Bioconcentration is the process by which there is a net accumulation of a chemical directly from water into the aquatic organisms. Biomagnification is the result of bioconcentration and bioaccumulation and implies a transfer of the chemical from food to consumer, so that residue concentrations increase systematically from one trophic level to the next.

A background plant-tissue sample collected for plants at site 2 proved to be a different species of pond weed (*Potamogeton*) than at sites 3 and 5, provides little information for comparison, and was not included in graphical or statistical analyses. A comparison of mean concentrations of selected trace metals for bed sediments and plants is shown in figure 5. With the exception of silver, trace-metal concentrations in plants that were collected are slightly larger than concentrations in the bed sediments, indicating that the plants are taking up these trace metals from the water and sediments. Although the metals are accumulated in plant tissue, concentrations generally are of the same order of magnitude and are not biomagnified.

The limited sampling of plants for this study does not address differences that may occur due to longer growing seasons downstream than upstream, variations in fine-grained sediments, or the influence of increases of such constituents as chloride, sulfate, and hardness in the downstream direction. Plants appeared healthy in all three locations, but were most abundant and longer stemmed downstream of the WWTP effluent. This probably is related to the warmer water

temperature and larger nutrient levels that result from the WWTP effluent (Freeman and Komar, 1991).

Three fish-tissue samples, consisting of liver-tissue composites from five fish of approximately the same weight, length, and age, were collected at both sites 3 and 5. Mean fish weight in relation to fish-liver tissue concentration of selected trace metals, shown in figure 6, indicates that there was no clear trend of increasing metal concentrations with the size (age) of the fish. There was an increase in concentration from the small size group to the medium size group, but a decrease in concentration from the medium to large size groups. If the fish were bioaccumulating these metals, then the concentration would be expected to increase with increasing size (age) grouping. Active biomagnification does not appear to occur with these metals in Rapid Creek biota; the concentrations of these trace metals in fish-liver tissue generally are of the same order of magnitude as the concentrations in bed sediments and plants.

Silver concentration increased in fish-liver tissue from upstream of the WWTP to downstream of the WWTP, copper and zinc generally decreased, and cadmium was essentially equal (figs. 4 and 6). Fish could potentially move from one site to another. If this were the case, then concentrations of metals in liver tissue would have been similar both upstream of the WWTP and downstream of the WWTP and the fish could be assumed to come from the same group. Differences in metal concentrations suggest that the fish are not moving between sites upstream of the WWTP and downstream of the WWTP.

A comparison of mean plant-tissue concentrations and mean fish-liver tissue concentrations for selected metals is shown in figure 7. Plant and fish-liver concentrations are similar with a tendency for metal concentrations in plants to be larger than in fish liver.

A comparison of mean concentrations of trace metals in bed sediment to mean concentrations in fish-liver tissue is shown in figure 8. Fish and sediment concentrations are similar with a tendency for metal concentrations in fish to be larger than in sediments upstream of the WWTP and metal concentrations in fish to be smaller than in sediments downstream of the WWTP. Because all of the fish were white suckers, which are benthic feeders, both plant and bed-sediment concentrations could affect metal concentrations in fish. The pathway for bioaccumulation could be either through uptake across the gills or through food sources

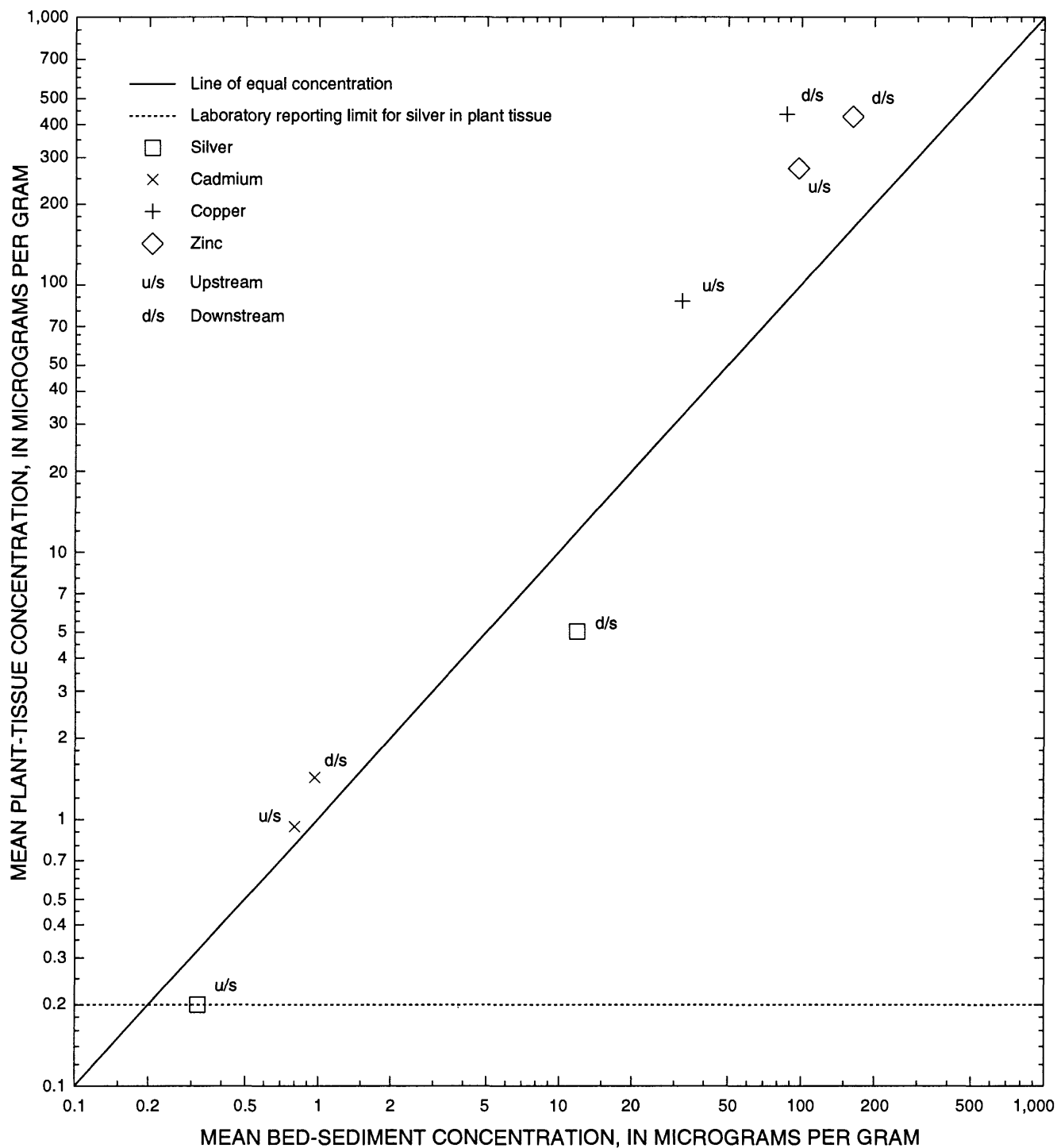


Figure 5. Comparison of mean concentrations of selected trace metals in bed sediments and plants upstream and downstream of the Waste Water Treatment Plant.

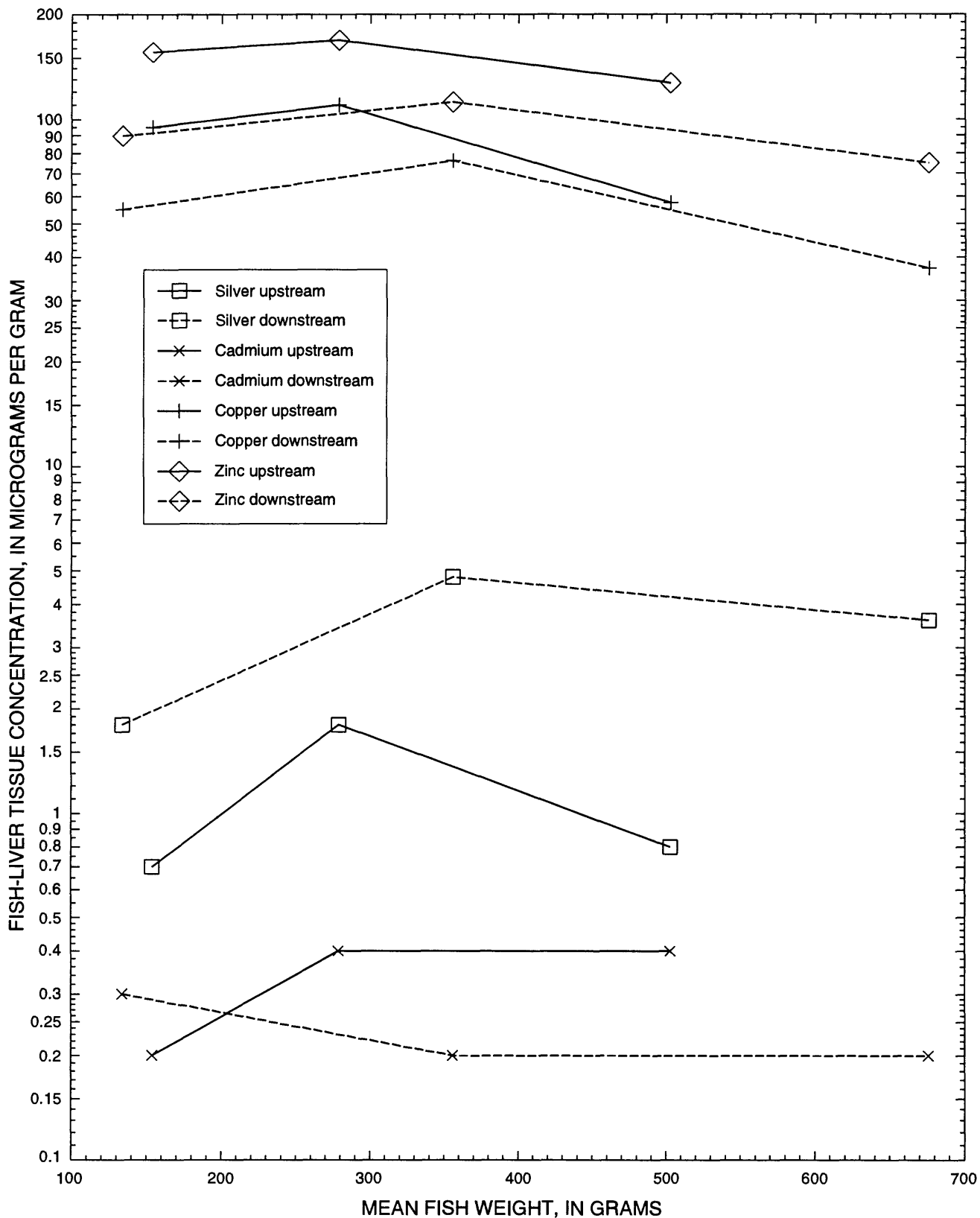


Figure 6. Mean fish weight in relation to concentration of selected trace metals in fish-liver tissue upstream and downstream of the Waste Water Treatment Plant.

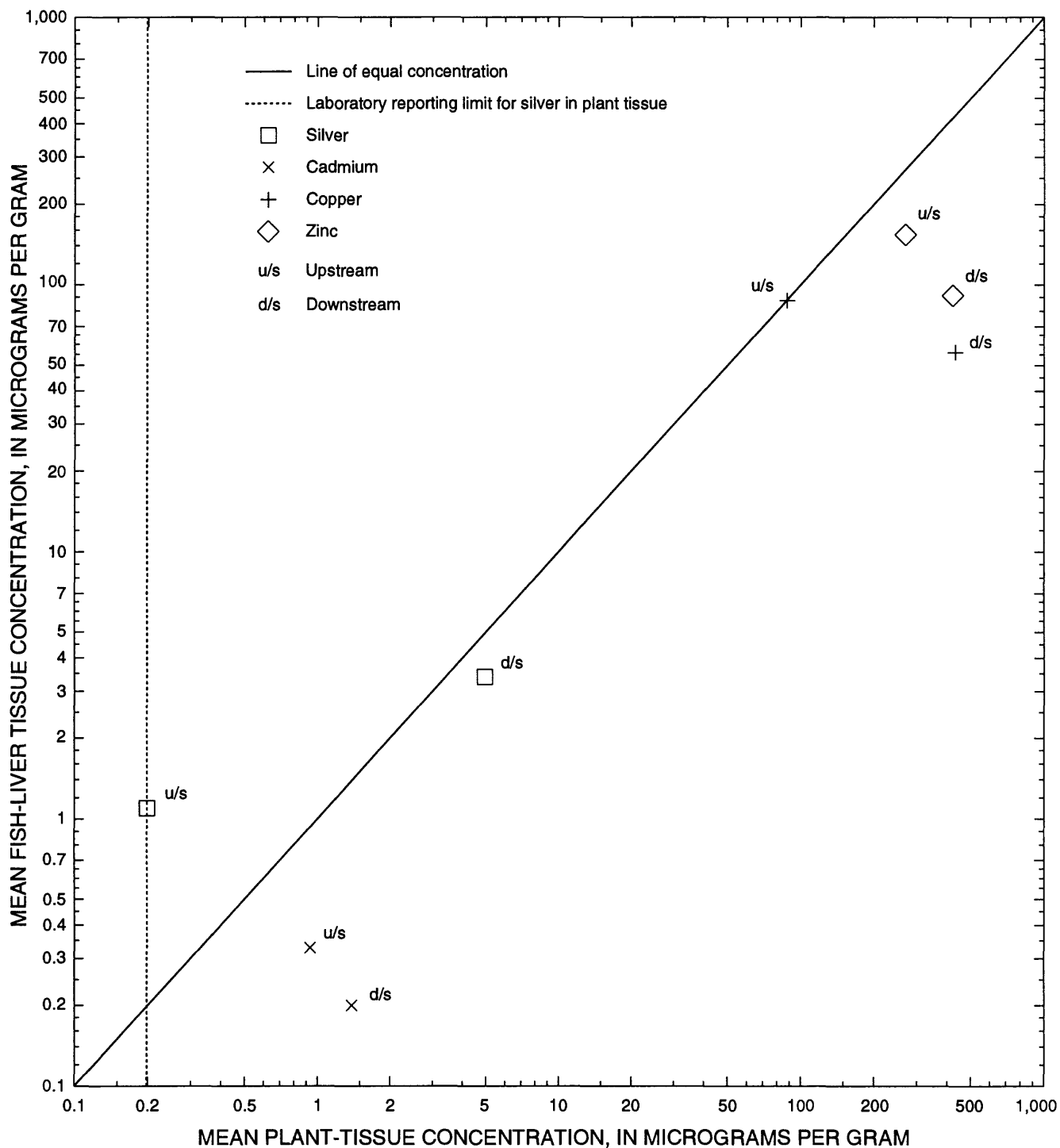


Figure 7. Comparison of mean concentrations of selected trace metals in plants and fish-liver tissue upstream and downstream of the Waste Water Treatment Plant.

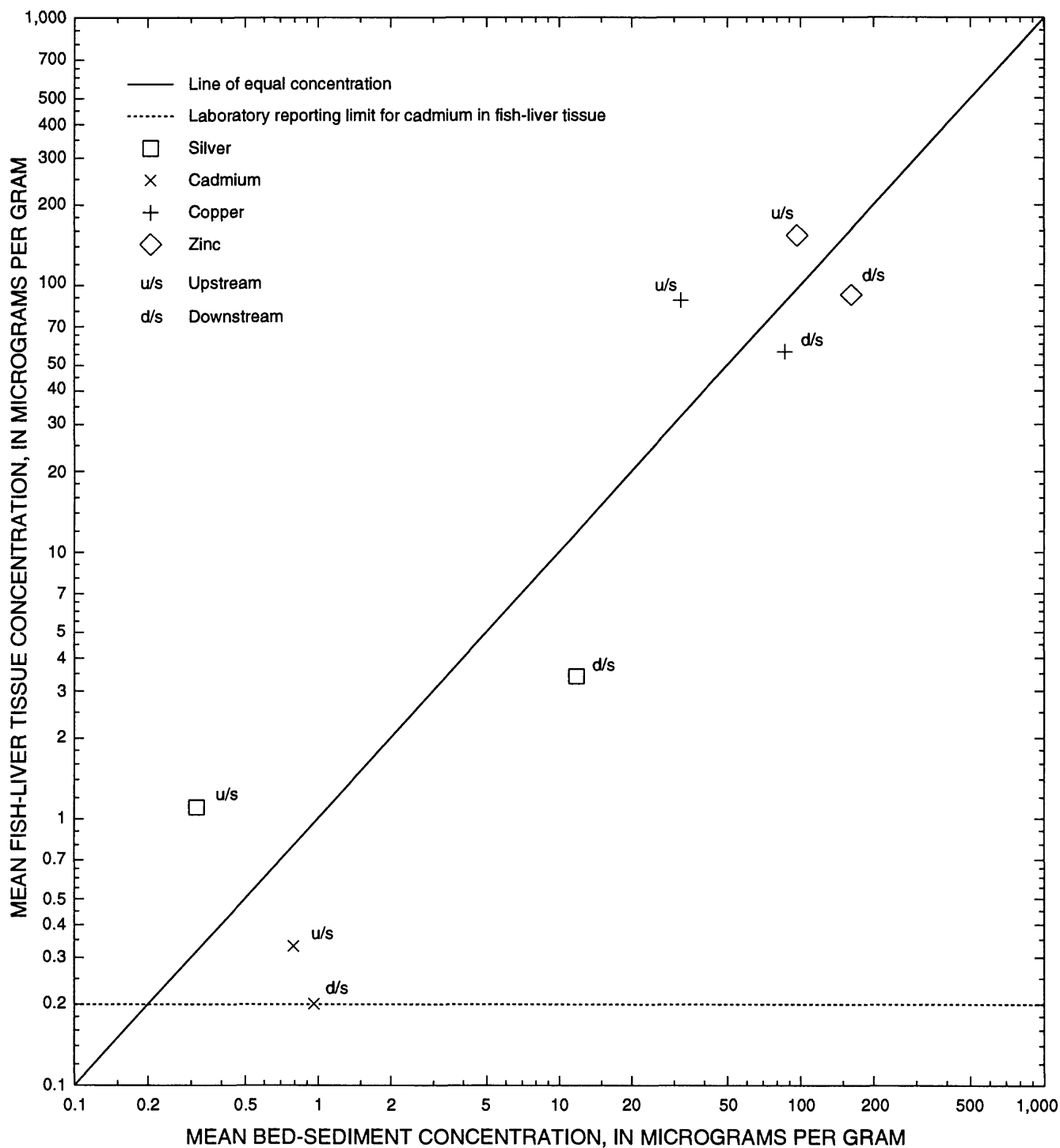


Figure 8. Comparison of mean concentrations of selected trace metals in bed sediments and fish-liver tissue upstream and downstream of the Waste Water Treatment Plant.

such as benthic invertebrates and plant material. The decrease in metal concentrations from the medium size groups to the large sized fish groups suggest that this species has the ability to remove trace metals from their bodies or that the amount of trace metals accumulated is finite and the concentration can be reduced by growth. In either case, the decrease in metal concentration from the medium size groups to the large size groups indicates a mechanism for reducing potential effects on this species. Examination of the fish indicated no abnormalities.

SUMMARY AND CONCLUSIONS

Various industries within Rapid City have National Pollutant Discharge Elimination System (NPDES) permits for discharging into the City sanitary-sewer system. Occasional violations of maximum contaminant levels were found by local industries and reported to the City. The industries requested that the City investigate whether natural concentrations of trace metals in the municipal water supply were contributing to concentrations of trace metals in the industrial effluent. An investigation was performed to determine background concentrations of trace metals in stream water, bed sediment, plants, and fish to better understand the aquatic conditions of Rapid Creek.

Water-quality sampling was conducted at three sites along Rapid Creek and additionally at the wastewater treatment plant effluent, at two deep wells that are part of the City water supply, at one of the City's infiltration galleries, and at a natural spring within the City that had detectable levels of silver during earlier sampling under different methods. The spring discharges from the Madison aquifer, which also is a major source of water to the City water-supply system. Low-level, ultra-clean methods were used throughout the sampling program to ensure accurate results. Silver concentrations were below the laboratory reporting limits for all Rapid Creek samples upstream of the WWTP and at the four additional sites. Concentrations in two samples at the site immediately downstream of the WWTP were 0.3 and 0.5 µg/L for dissolved silver and less than or equal to the laboratory reporting limit of 1 µg/L for total recoverable silver. Cadmium concentrations were all at or less than the laboratory reporting limit for all sites. Copper concentrations were at or relatively close to the laboratory reporting limit for sites upstream of the WWTP effluent and at the spring site, but were detectable at higher concentra-

tions at the remaining five sites. Zinc concentrations were detectable at all sites except the spring site.

Bed-sediment samples were collected at three sites along Rapid Creek, two sites upstream of the WWTP, and one immediately downstream of the WWTP. Silver, cadmium, copper, and zinc concentrations all increased from upstream of the WWTP to downstream of the WWTP.

Plant-tissue samples were collected at the same three sites along Rapid Creek as bed-sediment samples. Concentrations of silver, cadmium, copper, and zinc all increased from upstream of the WWTP to downstream of the WWTP and were consistent with increased concentrations in both stream water and bed sediments.

Fish were collected at two sites along Rapid Creek, one upstream of the WWTP, and one downstream of the WWTP. Fifteen fish were collected at each site, divided into three weight and length-determined groups, and liver tissue was collected for analysis of composite samples. Silver concentrations in fish liver were smaller upstream of the WWTP than downstream of the WWTP, with the largest concentration upstream being equal to the smallest concentration downstream. Cadmium concentrations varied little between sites. Copper and zinc concentrations were larger upstream of the WWTP than downstream of the WWTP.

Based on the limited sampling, there is evidence that the selected metals present in both the stream water and bed sediments are bioaccumulating in the plant and fish species collected in this study. Results also indicate that biomagnification in the plants and fish is not occurring at this time; that is, the concentrations found in the sediment, plants, and fish are all currently at approximately the same level of magnitude.

Based on the concentrations found in the water-quality, bed-sediment, plant, and fish sampling, there is an increase in the mean concentrations of selected trace metals from upstream of Rapid City to downstream of the WWTP effluent. Increases in concentrations from immediately upstream of the WWTP to downstream of the WWTP are consistent with concentrations added by the WWTP effluent. Bed-sediment concentrations of silver and cadmium increased between sites 2 and 3, and additional sampling would be necessary to determine possible point sources of trace metals in Rapid Creek upstream of the WWTP. Exceptions to increasing concentrations were copper and zinc in fish-liver tissue, which decreased from upstream of the WWTP effluent to downstream of the WWTP effluent.

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SUPPLEMENTAL DATA

Table 4. Water-quality data for sites along and near Rapid Creek, 1993-94

[US/CM, microsiemens per centimeter; MM, millimeters; MG/L, milligrams per liter; UG/L, micrograms per liter; --, no data available]

DATE	TIME	DIS- CHARGE, INST. CUBIC FEET PER SECOND (00061)	SPE- CIFIC CON- DUCT- ANCE (US/CM) (00095)	PH WATER FIELD (STAND- ARD UNITS) (00400)	TEMPER- ATURE AIR (DEG C) (00020)	TEMPER- ATURE WATER (DEG C) (00010)	BARO- METRIC PRES- SURE (MM HG) (00025)	OXYGEN, DIS- SOLVED (MG/L) (00300)	HARD- NESS TOTAL (MG/L CACO3) (00900)	ALKA- LITY LAB (MG/L CACO3) (90410)	SOLIDS, SUM OF CONSTI- TUENTS, DIS- SOLVED (MG/L) (70301)
Site 1, Station 06412500, Rapid Creek above Canyon Lake, near Rapid City											
JUL 1993											
¹ 06...	0800	--	1	9.0	15.0	9.0	--	--	--	2.6	--
06...	0845	207	376	8.4	15.0	9.0	670	11.4	190	150	207
² 06...	0930	--	1	6.4	15.0	9.0	--	--	--	2.7	--
JAN 1994											
¹ 24...	0600	--	2	9.1	18.5	19.0	--	--	--	1.2	--
24...	0700	30	359	8.3	-3.5	0.0	670	11.7	170	149	196
24...	1100	30	359	8.2	-2.0	0.0	670	12.5	170	149	196
24...	1500	30	357	8.3	-4.0	0.5	670	12.5	180	148	197
³ 24...	1501	30	357	8.3	-4.0	0.5	670	12.5	170	148	195
24...	1900	30	356	8.2	-2.5	0.5	670	12.1	170	148	194
24...	2300	30	356	8.1	-5.0	0.0	670	12.1	170	148	195
25...	0300	30	358	8.3	-4.5	0.0	670	12.1	170	149	195
AUG											
¹ 22...	0620	--	3	8.2	23.5	24.0	--	--	--	1.3	--
22...	0745	54	353	7.9	20.5	14.0	657	8.4	170	144	190
Site 3, Station 440126103054701 Rapid Creek above Sewage Treatment Plant, near Rapid City											
JUL 1993											
06...	1145	194	469	8.4	17.5	14.5	682	12.4	230	160	268
JAN 1994											
² 26...	0545	--	5	8.0	19.0	18.5	--	--	--	3.6	--
26...	0700	49	631	7.8	-6.5	0.0	684	10.7	300	183	378
26...	1100	49	630	8.0	-4.5	0.0	684	11.1	300	184	379
26...	1500	49	630	8.0	-5.0	0.0	681	11.6	300	183	379
³ 26...	1501	49	630	8.0	-5.0	0.0	681	11.6	290	184	378
26...	1900	49	633	8.0	-7.0	0.0	682	11.7	300	185	378
26...	2300	49	629	8.0	-7.5	0.0	682	11.6	300	185	378
27...	0300	49	627	8.0	-7.5	0.0	682	11.4	300	185	378
AUG											
24...	1345	25	622	8.2	30.0	22.5	674	11.1	300	176	380
OCT											
06...	0930	52	796	7.9	14.5	14.0	--	6.8	380	207	489
Site 4, Station 440124103054601 Sewage Treatment Plant effluent near Rapid City											
AUG 1994											
24...	0915	15	1260	7.3	21.5	19.0	673	4.4	360	191	701
Site 5, Station 06418900 Rapid Creek below Sewage Treatment Plant, near Rapid City											
AUG 1994											
³ 24...	0730	34	800	7.5	13.5	19.0	673	6.6	320	183	460
24...	0731	34	800	7.5	13.5	19.0	673	6.6	320	186	462
OCT											
06...	1130	71	1010	7.8	13.0	16.5	--	6.1	370	198	585
Site 6, Station 440343103163002 Meadowbrook Gallery at number 4 pumphouse											
AUG 1994											
³ 22...	1145	--	676	7.2	33.5	12.0	658	4.1	330	229	388
22...	1146	--	676	7.2	33.5	12.0	658	4.1	330	229	386
Site 7, Station 06413600 City Springs at Rapid City											
JUL 1994											
08...	1340	0.34	442	7.3	31.5	10.5	657	6.8	220	196	233
Site 8, Station 440342103160701 Well RC 9 completed in the Madison aquifer											
AUG 1994											
³ 25...	1145	--	370	7.6	31.0	16.5	664	7.4	170	162	194
25...	1146	--	370	7.6	31.0	16.5	664	7.4	170	162	193
Site 9, Station 440612103152001 Well RC 10 completed in the Madison aquifer											
AUG 1994											
25...	1315	--	343	7.5	30.5	15.5	661	--	170	171	176

¹Equipment blank.

²Field blank.

³Split.

Table 4. Water-quality data for sites along and near Rapid Creek, 1993-94—Continued

DATE	CALCIUM DIS- SOLVED (MG/L AS CA) (00915)	MAGNE- SIUM, DIS- SOLVED (MG/L AS MG) (00925)	SODIUM, DIS- SOLVED (MG/L AS NA) (00930)	SODIUM PERCENT (00932)	SODIUM AD- SORP- TION RATIO (00931)	POTAS- SIUM, DIS- SOLVED (MG/L AS K) (00935)	SULFATE DIS- SOLVED (MG/L AS SO4) (00945)	CHLO- RIDE, DIS- SOLVED (MG/L AS CL) (00940)	FLUO- RIDE, DIS- SOLVED (MG/L AS F) (00950)	NITRO- GEN, AMMONIA DIS- SOLVED (MG/L AS N) (00608)	CADMIUM TOTAL RECOV- ERABLE (UG/L AS CD) (01027)
Site 1, Station 06412500, Rapid Creek above Canyon Lake, near Rapid City											
JUL 1993											
¹ 06...	0.02	<0.01	<0.20	--	--	<0.10	<0.10	0.40	<0.10	0.020	<1
06...	40	21	3.8	4	0.1	3.1	46	3.0	0.30	0.020	<1
² 06...	0.03	<0.01	<0.20	--	--	<0.10	0.20	<0.10	<0.10	0.020	<1
JAN 1994											
¹ 24...	<0.02	<0.01	<0.20	--	--	<0.10	<0.10	<0.10	<0.10	0.010	<1
24...	39	18	4.2	5	0.1	2.6	39	3.7	0.20	0.010	<1
24...	39	18	4.1	5	0.1	2.6	39	3.7	0.30	0.010	<1
24...	39	19	4.2	5	0.1	2.6	39	3.8	0.20	0.010	<1
³ 24...	39	18	4.1	5	0.1	2.6	39	3.7	0.20	0.010	<1
24...	38	18	4.1	5	0.1	2.5	39	3.8	0.20	0.010	<1
24...	38	18	4.1	5	0.1	2.5	39	4.0	0.20	0.010	<1
25...	38	18	4.0	5	0.1	2.5	39	3.9	0.20	0.010	<1
AUG											
¹ 22...	<0.02	<0.01	<0.20	--	--	0.40	<0.10	0.20	<0.10	<0.010	<1
22...	39	18	3.6	4	0.1	2.4	38	2.6	0.20	0.010	<1
Site 3, Station 440126103054701 Rapid Creek above Sewage Treatment Plant, near Rapid City											
JUL 1993											
06...	53	24	5.9	5	0.2	3.3	81	4.9	0.30	0.030	<1
JAN 1994											
² 26...	0.02	<0.01	<0.20	--	--	<0.10	<0.10	0.20	<0.10	0.010	<1
26...	72	28	12	8	0.3	3.2	140	13	0.30	0.020	<1
26...	72	28	12	8	0.3	3.2	140	13	0.30	0.020	<1
26...	73	28	12	8	0.3	3.2	140	13	0.30	0.020	<1
³ 26...	71	28	12	8	0.3	3.2	140	13	0.30	0.020	<1
26...	72	28	11	7	0.3	3.1	140	13	0.30	0.010	<1
26...	72	28	11	7	0.3	3.2	140	13	0.30	0.020	<1
27...	72	28	11	7	0.3	3.3	140	12	0.30	0.020	<1
AUG											
24...	69	32	12	8	0.3	3.2	150	7.5	0.30	0.020	<1
OCT											
06...	92	36	18	9	0.4	5.5	200	13	0.40	<0.015	<1
Site 4, Station 440124103054601 Sewage Treatment Plant effluent near Rapid City											
AUG 1994											
24...	88	34	120	41	3	12	190	140	1.3	0.590	<1
Site 5, Station 06418900 Rapid Creek below Sewage Treatment Plant, near Rapid City											
AUG 1994											
24...	75	33	37	20	0.9	5.2	160	39	0.50	0.200	--
³ 24...	75	33	37	20	0.9	5.2	160	39	0.50	0.200	<1
OCT											
06...	90	35	60	26	1	8.9	200	71	0.80	0.400	<1
Site 6, Station 440343103163002 Meadowbrook Gallery at number 4 pumphouse											
AUG 1994											
22...	87	28	9.1	6	0.2	3.5	110	13	0.20	0.020	<1
³ 22...	85	28	8.9	6	0.2	3.5	110	13	0.20	0.020	<1
Site 7, Station 06413600 City Springs at Rapid City											
JUL 1994											
08...	54	20	4.2	4	0.1	2.1	30	5.1	0.20	0.020	<1
Site 8, Station 440342103160701 Well RC 9 completed in the Madison aquifer											
AUG 1994											
25...	40	18	5.9	7	0.2	2.3	26	4.7	0.30	0.010	<1
³ 25...	40	18	5.8	7	0.2	2.5	25	3.9	0.20	<0.010	<1
Site 9, Station 440612103152001 Well RC 10 completed in the Madison aquifer											
AUG 1994											
25...	38	19	2.6	3	0.1	1.6	11	1.0	0.20	<0.010	<1

¹Equipment blank.

²Field blank.

³Split.

Table 4. Water-quality data for sites along and near Rapid Creek, 1993-94—Continued

DATE	CADMIUM DIS- SOLVED (UG/L AS CD) (01025)	COPPER, TOTAL RECOV- ERABLE (UG/L AS CU) (01042)	COPPER, DIS- SOLVED (UG/L AS CU) (01040)	MANGA- NESE, DIS- SOLVED (UG/L AS MN) (01056)	SILVER, TOTAL RECOV- ERABLE (UG/L AS AG) (01077)	SILVER, DIS- SOLVED (UG/L AS AG) (01075)	ZINC, TOTAL RECOV- ERABLE (UG/L AS ZN) (01092)	ZINC, DIS- SOLVED (UG/L AS ZN) (01090)	MERCURY TOTAL RECOV- ERABLE (UG/L AS HG) (71900)	MEDIUM CODE
Site 1, Station 06412500, Rapid Creek above Canyon Lake, near Rapid City										
JUL 1993										
¹ 06...	<0.1	<1	<1	0.3	<1	--	<10	<1	<0.10	Q
06...	0.1	1	<1	5.0	<1	<0.2	<10	<1	<0.10	9
² 06...	<0.1	<1	<1	<0.2	<1	--	<10	1	<0.10	Q
JAN 1994										
¹ 24...	<0.1	<1	<1	<0.2	<1	<0.2	10	<1	<0.10	Q
24...	<0.1	<1	<1	0.6	<1	<0.2	<10	<1	<0.10	9
24...	<0.1	<1	<1	0.6	<1	<0.2	<10	3	<0.10	9
24...	<0.1	<1	<1	0.6	<1	<0.2	<10	1	<0.10	9
³ 24...	<0.1	<1	<1	0.6	<1	<0.2	<10	1	<0.10	Q
24...	<0.1	<1	<1	0.5	<1	<0.2	<10	1	<0.10	9
24...	<0.1	<1	<1	0.9	<1	<0.2	<10	3	<0.10	9
25...	<0.1	<1	<1	0.5	<1	<0.2	<10	3	<0.10	9
AUG										
¹ 22...	<0.1	<1	<1	0.3	<1	<0.2	<10	<1	<0.10	Q
22...	<0.1	<1	<1	1.9	<1	<0.2	<10	1	<0.10	9
Site 3, Station 440126103054701 Rapid Creek above Sewage Treatment Plant, near Rapid City										
JUL 1993										
06...	<0.1	3	<1	13	<1	<0.2	10	<1	<0.10	9
JAN 1994										
² 26...	<0.1	<1	<1	<0.2	<1	<0.2	<10	<1	<0.10	Q
26...	<0.1	<1	<1	6.4	<1	<0.2	<10	1	<0.10	9
26...	<0.1	<1	<1	6.7	<1	<0.2	<10	1	<0.10	9
26...	<0.1	<1	<1	6.5	<1	<0.2	<10	2	<0.10	9
³ 26...	<0.1	<1	<1	6.4	<1	<0.2	<10	2	<0.10	Q
26...	<0.1	<1	<1	6.1	<1	<0.2	<10	5	<0.10	9
26...	<0.1	<1	<1	6.2	<1	<0.2	<10	2	<0.10	9
27...	<0.1	<1	<1	6.2	<1	<0.2	<10	1	<0.10	9
AUG										
24...	<0.1	<1	1	19	<1	<0.2	20	<1	<0.10	9
OCT										
06...	<0.1	2	<1	34	<1	<0.2	<10	3	<0.10	9
Site 4, Station 440124103054601 Sewage Treatment Plant effluent near Rapid City										
AUG 1994										
24...	0.1	16	13	59	5	2.4	40	29	<0.10	9
Site 5, Station 06418900 Rapid Creek below Sewage Treatment Plant, near Rapid City										
AUG 1994										
24...	<0.1	4	4	35	<1	0.3	10	5	<0.10	9
³ 24...	<0.1	5	3	34	1	0.3	10	5	<0.10	R
OCT										
06...	<0.1	9	5	40	1	0.5	<20	14	<0.10	9
Site 6, Station 440343103163002 Meadowbrook Gallery at number 4 pumphouse										
AUG 1994										
22...	<0.1	11	2	<0.2	<1	<0.2	<10	1	<0.10	9
³ 22...	<0.1	7	2	<0.2	<1	<0.2	<10	1	<0.10	R
Site 7, Station 06413600 City Springs at Rapid City										
JUL 1994										
08...	<0.1	<1	<1	<0.2	<1	<0.2	<10	<1	<0.10	9
Site 8, Station 440342103160701 Well RC 9 completed in the Madison aquifer										
AUG 1994										
25...	<0.1	3	3	1.1	<1	<0.2	<10	5	<0.10	6
³ 25...	<0.1	3	3	0.7	<1	<0.2	<10	7	<0.10	S
Site 9, Station 440612103152001 Well RC 10 completed in the Madison aquifer										
AUG 1994										
25...	<0.1	21	2	0.6	<1	<0.2	10	10	<0.10	6

¹Equipment blank.

²Field blank.

³Split.

Table 5. Chemical analyses of bed sediments for sites along Rapid Creek, 1993-94

Site number	Field number	Concentration, in percent							
		Aluminum	Calcium	Iron	Potassium	Magnesium	Sodium	Phosphorus	Titanium
2	C-A	5.0	8.8	2.9	2.0	1.9	0.36	0.11	0.25
¹ 2	C-B	4.8	8.7	2.9	1.9	1.9	.36	.11	.25
3	A-1	5.2	11	2.6	1.6	1.3	.32	.11	.24
3	A-2	5.0	11	2.7	1.6	1.3	.31	.11	.23
3	A-3	5.1	12	2.5	1.6	1.3	.31	.09	.24
5	B-1	5.1	8.4	2.7	1.6	1.3	.38	.34	.27
5	B-2	5.8	6.7	3.1	1.8	1.3	.38	.20	.28
5	B-3-A	6.0	6.2	3.0	1.7	1.3	.32	.24	.28
¹ 5	B-3-B	5.8	6.6	3.1	1.8	1.3	.37	.21	.28

Table 5. Chemical analyses of bed sediments for sites along Rapid Creek, 1993-94—Continued

Site number	Concentration, in micrograms per gram										
	Manganese	Silver	Silver (low level)	Arsenic	Gold	Barium	Beryllium	Bismuth	Cadmium	Cadmium (low level)	Cerium
2	440	<2	0.18	17	<8	440	1	<10	<2	0.47	62
¹ 2	440	<2	.18	20	<8	450	1	<10	<2	.50	61
3	480	<2	.41	17	<8	430	2	<10	<2	.91	56
3	570	<2	.39	18	<8	430	2	<10	<2	.90	54
3	540	<2	.30	14	<8	420	2	<10	<2	.90	54
5	560	18	19	13	<8	630	2	<10	<2	.96	62
5	560	7	6.9	15	<8	530	2	<10	<2	.97	68
5	540	10	9.8	12	<8	520	2	<10	<2	.98	64
¹ 5	570	7	7.1	10	<8	510	2	<10	<2	.96	69

Table 5. Chemical analyses of bed sediments for sites along Rapid Creek, 1993-94—Continued

Site number	Concentration, in micrograms per gram										
	Cobalt	Chromium	Copper	Europium	Gallium	Homium	Lanthanum	Lithium	Molybdenum	Niobium	Neodymium
2	10	58	31	<2	8	<4	31	37	<2	5	24
¹ 2	10	56	31	<2	10	<4	32	35	<2	6	24
3	10	56	35	<2	10	<4	29	35	<2	7	21
3	9	58	31	<2	11	<4	28	34	<2	7	21
3	9	59	32	<2	11	<4	28	34	<2	7	19
5	10	62	110	<2	10	<4	32	33	<2	7	30
5	10	72	67	<2	14	<4	36	39	<2	7	29
5	11	74	84	<2	15	<4	33	40	<2	10	26
¹ 5	12	72	68	<2	13	<4	35	39	2	8	27

Table 5. Chemical analyses of bed-sediments for sites along Rapid Creek, 1993-94—Continued

Site number	Concentration, in micrograms per gram											
	Nickel	Lead	Scandium	Tin	Strontium	Tantalum	Thorium	Uranium	Vanadium	Yttrium	Ytterbium	Zinc
2	29	40	7	<5	230	<40	8	<100	74	17	2	120
¹ 2	29	39	7	<5	230	<40	8	<100	74	18	2	120
3	28	39	8	<5	330	<40	7	<100	100	18	2	130
3	26	36	8	<5	340	<40	6	<100	100	17	2	130
3	27	43	7	<5	360	<40	6	<100	96	19	2	130
5	30	36	8	<5	340	<40	9	<100	95	21	2	160
5	33	52	9	<5	270	<40	11	<100	110	25	2	160
5	31	48	9	<5	260	<40	11	<100	110	21	2	170
¹ 5	32	49	9	<5	260	<40	9	<100	110	21	2	160

¹Split sample.

Table 6. Chemical analyses of plant tissue for sites along Rapid Creek, 1993-94

Site number	Field number	Concentration, in percent							
		Aluminum	Calcium	Iron	Potassium	Magnesium	Sodium	Phosphorus	Titanium
2	C-1	0.35	9.0	0.66	23	3.3	3.4	1.3	0.01
3	V-1	1.0	9.7	1.2	18	2.2	5.9	1.8	.05
3	V-2	0.80	11	1.4	17	2.1	6.2	1.7	.03
3	V-3	0.69	16	1.5	16	2.4	4.3	1.9	.03
5	D-1	0.43	8.7	2.7	21	2.1	4.1	5.7	.02
5	D-2	0.65	8.9	3.2	15	2.3	3.5	5.2	.03
5	D-3	0.52	10	1.9	19	2.4	3.4	5.1	.02

Table 6. Chemical analyses of plant tissue for sites along Rapid Creek, 1993-94—Continued

Site number	Concentration, in micrograms per gram										
	Manganese	Silver	Silver (low level)	Arsenic	Gold	Barium	Beryllium	Bismuth	Cadmium	Cadmium (low level)	Cerium
2	7,000	<4	<0.20	<20	<20	380	<2	<20	<4	1.6	8
3	5,700	<4	<.20	26	<20	330	<2	<20	<4	.80	13
3	5,900	<4	<.20	26	<20	340	<2	<20	<4	.92	9
3	9,900	<4	<.20	30	<20	580	<2	<20	<4	1.1	12
5	5,600	<4	4.2	<20	<20	660	<2	<20	<4	1.4	<8
5	5,900	5	5.5	28	<20	830	<2	<20	<4	1.2	9
5	5,100	6	5.4	<20	<10	650	<2	<20	<4	1.7	<7

Table 6. Chemical analyses of plant tissue for sites along Rapid Creek, 1993-94—Continued

Site number	Concentration, in micrograms per gram										
	Cobalt	Chromium	Copper	Europium	Gallium	Holmium	Lanthanum	Lithium	Molybdenum	Niobium	Neodymium
2	14	5	250	<4	12	<8	<4	7	6	<8	<8
3	13	12	63	<4	9	<8	8	15	<4	<8	<8
3	19	9	78	<4	9	<8	6	15	<4	<8	<8
3	27	6	120	<4	<8	<8	6	11	<4	<8	<8
5	11	9	430	<4	<8	<8	4	9	<4	<8	<8
5	10	9	410	<4	<7	<7	<4	8	<4	<7	<7
5	10	8	470	<4	<7	<7	5	8	<4	<7	<7

Table 6. Chemical analyses of plant tissue for sites along Rapid Creek, 1993-94—Continued

Site number	Concentration, in micrograms per gram												Concentration, in percent
	Nickel	Lead	Scandium	Tin	Strontium	Tantalum	Thorium	Uranium	Vanadium	Yttrium	Ytterbium	Zinc	Ash
2	27	18	<4	<10	530	<80	<8	<200	17	<4	<2	550	16.7
3	24	13	<4	<10	670	<80	<8	<200	27	4	<2	230	23.9
3	26	19	<4	<10	810	<80	<8	<200	26	<4	<2	260	23.0
3	35	20	<4	<10	1,100	<80	9	<200	29	4	<2	330	16.7
5	20	11	<4	<9	970	<80	<8	<200	13	<4	<2	430	20.6
5	22	15	<4	<9	980	<70	7	<200	17	4	<2	430	21.5
5	21	17	<4	<9	1,000	<70	<7	<200	18	<4	<2	420	17.5

Table 7. Chemical analyses of fish-liver tissue for sites along Rapid Creek, 1993-94

[UG/G, micrograms per gram]

DATE	SIZE	ALUMI- NUM, BIO TIS LIVER, DRY WGT REC (UG/G) (49237)	BARIUM, BIOTA, TISSUE, LIVER, DRY WGT REC (UG/G) (49238)	BORON, BIOTA, TISSUE, LIVER, DRY WGT REC (UG/G) (49239)	CHROM- IUM- BIO TIS LIVER, DRY WGT REC (UG/G) (49240)	COPPER, BIOTA, TISSUE, LIVER, DRY WGT REC (UG/G) (49241)	IRON, BIOTA, TISSUE, LIVER, DRY WGT REC (UG/G) (49242)	MANGAN- ESE, BIO TIS LIVER, DRY WGT REC (UG/G) (49243)	STRON- TIUM, BIO TIS LIVER, DRY WGT REC (UG/G) (49244)	ZINC, BIOTA, TISSUE, LIVER, DRY WGT REC (UG/G) (49245)	ANTI- MONY, BIO TIS LIVER, DRY WGT REC (UG/G) (49246)	ARSENIC BIOTA, TISSUE, LIVER, DRY WGT REC (UG/G) (49247)
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Site 3, Station 440126103054701 Rapid Creek above Sewage Treatment Plant, near Rapid City

OCT 1994

06...	Small	11	0.2	0.3	0.6	95	480	9.2	0.8	160	<0.2	<0.2
06...	Medium	<1.0	<0.1	0.4	0.6	110	470	9.8	0.6	170	<0.3	<0.3
06...	Large	1.5	0.1	0.2	0.6	58	790	12	1.1	130	<0.3	<0.3

Site 5, Station 06418900 Rapid Creek below Sewage Treatment Plant, near Rapid City

OCT 1994

06...	Small	<1.0	<0.1	0.6	0.5	55	290	7.1	0.7	90	<0.3	<0.3
06...	Medium	<1.0	<0.1	1.1	0.5	76	300	7.0	0.6	110	<0.2	<0.2
06...	Large	1.9	<0.1	0.2	<0.5	37	590	6.0	0.4	75	<0.2	<0.2

Table 7. Chemical analyses of fish-liver tissue for sites along Rapid Creek, 1993-94—Continued

DATE	BERYL- LIUM- BIO TIS LIVER, DRY WGT REC (UG/G) (49248)	CADMIUM BIOTA, TISSUE, LIVER, DRY WGT REC (UG/G) (49249)	COBALT, BIOTA, TISSUE, LIVER, DRY WGT REC (UG/G) (49250)	LEAD, BIOTA, TISSUE, LIVER, DRY WGT REC (UG/G) (49251)	MOLYB- DENUM, BIO TIS LIVER, DRY WGT REC (UG/G) (49252)	NICKEL, BIOTA, TISSUE, LIVER, DRY WGT REC (UG/G) (49253)	SELEN- IUM, BIO TIS LIVER, DRY WGT REC (UG/G) (49254)	SILVER, BIOTA, TISSUE, LIVER, DRY WGT REC (UG/G) (49255)	URANIUM BIOTA, TISSUE, LIVER, DRY WGT REC (UG/G) (49257)	MERCURY BIOTA, TISSUE, LIVER, DRY WGT REC (UG/G) (49258)	WATER, PRESENT BIO TIS LIVER, DRY WGT REC (UG/G) (49273)	VANA- DIUM BIO TIS LIVER, DRY WGT REC (UG/G) (49465)
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Site 3, Station 440126103054701 Rapid Creek above Sewage Treatment Plant, near Rapid City

OCT 1994

06...	<0.2	0.2	0.3	<0.2	1.3	1.0	6.4	0.7	<0.2	0.1	78	0.3
06...	<0.3	0.4	<0.3	<0.3	1.4	0.6	6.4	1.8	<0.3	<0.1	80	<0.3
06...	<0.3	0.4	0.5	<0.3	1.2	0.9	6.4	0.8	<0.3	0.1	79	0.4

Site 5, Station 06418900 Rapid Creek below Sewage Treatment Plant, near Rapid City

OCT 1994

06...	<0.3	<0.3	<0.3	<0.3	0.9	0.7	7.3	1.8	<0.3	0.1	78	<0.3
06...	<0.2	<0.2	<0.2	<0.2	1.0	0.7	6.9	4.8	<0.2	0.2	79	<0.2
06...	<0.2	0.2	<0.2	<0.2	0.7	0.4	4.5	3.6	<0.2	0.2	71	<0.2